Olefin Insertion into the Platinum—Hydrogen Bond

By H. C. CLARK* and H. KUROSAWA

(*Department of Chemistry, University of Western Ontario, London, Canada*)

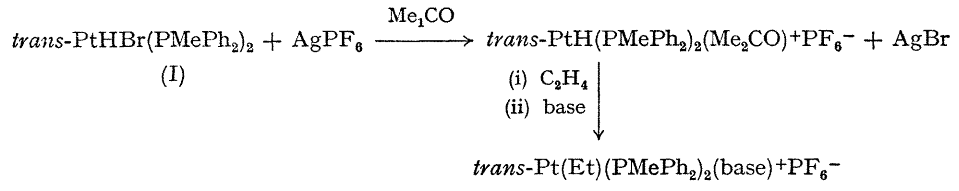
Summary Ready insertion of ethylene or propene into the Pt–H bond of $\mathrm{Pt^{II}}$ hydrido-complexes, which leads to good yields of ethyl or n-propyl derivatives, involves displacement of the ligand *trans* to the hydridic hydrogen in a cationic species, giving a cationic hydrido-olefin complex as intermediate.

CHATT and SHAW[1] reported the reversible addition of ethylene to *trans*-$\mathrm{PtHCl(PEt_3)_2}$ [reaction (1)] and the

$$\textit{trans}\text{-}\mathrm{PtHCl(PEt_3)_2} + \mathrm{C_2H_4} \rightleftharpoons \textit{trans}\text{-}\mathrm{Pt(Et)Cl(PEt_3)_2} \quad (1)$$

suggestion has been accepted[2,3] that both forward and reverse reactions proceed *via* five-co-ordinate π-olefinic complexes. The forward reaction required rather vigorous conditions[2] (95° and 80 atm pressure or more), but the equilibrium is established[4] within 30 min at 25° and 1 atm, in the presence of 1 mol % of tin(II) chloride ($K_{\mathrm{eq}} = 35\ \mathrm{l^{-1}\ mol}$.

We have now observed that reaction (2) takes place rapidly at 25° and 1 atm pressure. The base employed is 2,4,6-trimethylpyridine, carbon monoxide, or a carbene[5,6] of the type $:\overline{\mathrm{C}\cdot\mathrm{O}\cdot[\mathrm{CH_2}]_2\cdot\mathrm{C}}\mathrm{H_2}$. Moreover, a similar reaction with propene instead of ethylene also occurs readily as does the reaction of compound (I) with ethylene when $\mathrm{AgPF_6}$ is used in only catalytic amounts, giving good yields of *trans*-$\mathrm{Pt(Et)Br(PMePh_2)_2}$. The use of the silver salt, or rather the removal of bromide, in this case as silver bromide, is essential since no reaction occurs between compound (I) and ethylene in the absence of $\mathrm{AgPF_6}$ or in the presence of $\mathrm{NaPF_6}$. Nor did the cations *trans*-$\mathrm{[PtH(PMePh_2)_2L]^+}$ (L = 2,4,6-trimethylpyridine, $\mathrm{PMePh_2}$ or *p*-$\mathrm{MeC_6H_4NC}$) react with ethylene as in reaction (2).



$$\begin{array}{ccl} \textit{trans}\text{-}\mathrm{PtHBr(PMePh_2)_2} + \mathrm{AgPF_6} & \xrightarrow{\mathrm{Me_1CO}} & \textit{trans}\text{-}\mathrm{PtH(PMePh_2)_2(Me_2CO)^+PF_6^-} + \mathrm{AgBr} \\ \mathrm{(I)} & & \big\downarrow \text{(i) } \mathrm{C_2H_4}\ \text{(ii) base} \\ & & \textit{trans}\text{-}\mathrm{Pt(Et)(PMePh_2)_2(base)^+PF_6^-} \end{array} \quad (2)$$

The results suggest that platinum hydride insertions may readily be achieved by a cationic mechanism, that the ease of olefin insertion into the Pt–H bond is intimately related to the ease of displacement of the ligand *trans* to the hydridic hydrogen by olefin, and that the key intermediates in the insertion process are essentially four- and not five-co-ordinate. Thus, the results are consistent with the fact that ethylene will displace acetone, but not more strongly co-ordinating ligands such as pyridine, tertiary phosphine, or isocyanide in *trans*-$\mathrm{[PtMe(PMe_2Ph)_2L]^+}$, nor chloride in *trans*-$\mathrm{PtMeCl(PMe_2Ph)_2}$.[7] Similarly, reactions of *trans*-$\mathrm{[PtMe(PMe_2Ph)_2L]^+}$ with acetylenes,[8] allenes,[8] and perfluoroaryl nitriles[9] show carbonium ion reactivity *only* when L may be displaced by the unsaturated ligand. These conclusions are also consistent with the observed displacement[10] of nitrate by a diene or ethylene in a $\mathrm{Pt^{II}}$ complex.

In accord with this we also have found that *trans*-$\mathrm{PtH(NO_3)(PMePh_2)_2}$ reacts readily with ethylene in acetone or methylene chloride at 25° and 1 atm pressure to give the expected ethyl compound, *trans*-$\mathrm{Pt(Et)(NO_3)(PMePh_2)_2}$ in high yield. The catalysed reaction of (I) with ethylene may proceed by the equilibrium (3) where L = acetone or ethylene.

$$\textit{trans}\text{-}[\mathrm{Pt(Et)(PMePh_2)_2L}]^+ + (\mathrm{I}) \rightleftharpoons \textit{trans}\text{-}\mathrm{Pt(Et)Br\text{-}(PMePh_2)_2} + \textit{trans}\text{-}[\mathrm{Pt(PMePh_2)_2L}]^+ \qquad (3)$$

(*Received, May 24th,* 1971; *Com.* 830.)

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